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II.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON SODIC ZINCATES.

By Arthur M. Comey and C. Loring Jackson.

Presented June 13, 1888.

Although the solubility of zincic hydrate in alkalis is one of the most familiar facts in chemistry, very few attempts, so far as we can find, have been made to determine what compounds exist in such a solution. The reason for this is not far to seek, as the results obtained by the few who have studied this subject are so decidedly unsatisfactory, that they are not likely to induce others to take up this line of work.

The first important papers in this field appeared in the *Annalen der Chemie und Pharmacie* in 1834, having been brought out by a prize offered from the Hagen-Bucholz foundation for work on zincic oxide. Of the various competitors Laux,* who was most successful in his work on this part of the subject, found that a solution of zincic oxide in caustic alkali, if covered with a layer of alcohol, gradually deposited little shining crystals, which were easily soluble in water, and, he states, contained equal molecules of zincic oxide and the alkaline oxide (ZnO_2K_2). These crystals were decomposed by heat, giving a white powder, which contained one molecule of alkaline oxide to two of zincic oxide, but no analyses of either of these substances are given.

Two other competitors for this Hagen-Bucholz prize, Bonnet † and Sander,‡ also touch on this subject, but their results are of less importance. Sander, in fact, comes to the conclusion that no definite compound is formed when zincic oxide is dissolved in a caustic alkali.

The next paper on the subject was published in 1842, by Fremy, §

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* Ann. Chem. Pharm., ix. 183.

† Ibid., ix. 177.

‡ Ibid., ix. 181.

§ Comptes Rendus, xv. 1106.

who states that the compounds formed by zincic oxide and an alkali were in general deliquescent and amorphous, but by using a potassic hydrate solution of zincic oxide, and adding to it a small quantity of alcohol, long needles were obtained, which he considered a "bi-zincate of potassa." It was immediately decomposed by water into zincic oxide and potassic hydrate. A few years later, in his article in the *Annales de Chimie et de Physique*,* Fremy states that he has met with great difficulties in obtaining the crystals, and hopes to return to the subject when he has determined the conditions under which they are formed. Neither of his papers contains analyses, and he has never published anything more on the subject, the reason for which we can well understand after our unsuccessful attempts to prepare potassic zincates.

The work on the ammonic zincates has led to about the same unsatisfactory results, no analyses of laboratory products having been published; but Malaguti † gives an analysis of an incrustation found upon a brick in the vault of a privy, which had the composition $3ZnO . 4 NH_3 . 12 H_2O$.

The only other research which has approached this subject is one by Prescott,* published in 1880, on the solubility of zincic oxide in caustic alkalis. He found that more alkali is needed for complete solution of the zincic oxide than would be required by the following reaction,

$$ZnSO_4 + 4 KOH = Zn(OK)_2 + K_2SO_4 + 2 H_2O,$$

but this excess was smaller in the case of sodic or ammonic hydrate than with potassic hydrate; also that the excess of alkali could be neutralized in such a solution without precipitating zincic hydrate, until the amount was reached indicated by the reaction given above. Addition of a large quantity of water precipitated the zincic hydrate from the solution, even when it contained the excess of alkali. The effect of dilution and temperature on the solubility were also studied, but the determination of the composition of the substances formed did not come within the scheme of his work.

As, therefore, we could find in the chemical literature no analyses of a zincate, with the exception of Malaguti's ammonic zincate, we decided to take up the subject, and fortunately began our work with the sodic zincate, since this proved to be the one of them all which can be most easily prepared.

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* Ann. Chim. Phys., Ser. 3, xii.

† Comptes Rendus, lxii. 413.

‡ Chem. News, xlii. 30.

The principal results which we have obtained can be briefly summarized as follows. From a solution of zincic oxide in aqueous sodic hydrate two crystalline sodic zincates can be separated by the action of alcohol; the principal product, which fuses below 100°, has the formula $Zn_3O_6Na_4H_2 . 17 H_2O$, the other, which does not fuse at 300°, is $(ZnO_2NaH)_2 . 7 H_2O$. Both substances are decomposed into zincic oxide and sodic hydrate by water or alcohol. We had hoped at first to extend our work to other zincates, but, after a number of experiments, have abandoned this intention, as with potassic hydrate no crystalline or definite compound could be obtained, and, although ammonic hydrate gave a product crystallizing in needles, it was obtained with difficulty, and proved to be of varying composition. We give, however, at the end of this paper, a brief account of the negative results of these experiments, and of some others in similar directions.

Preparation of the Sodic Zincates.

The sodic zincates can be prepared by the action of sodic hydrate on either metallic zinc, zincic oxide, or zincic hydrate, and the product seemed to be the same in every case. It is most convenient, therefore, to prepare them from zincic oxide, as the metallic zinc dissolves very slowly, long boiling with aqueous sodic hydrate being necessary to prepare a sufficiently strong solution. On the other hand, we have not succeeded in preparing the sodic zincates from sodic carbonate, as a mixture of this substance with zincic oxide showed no loss of weight even when kept at a white heat for some time. The method adopted by us consisted in dissolving zincic oxide in a strong aqueous solution of sodic hydrate,* with the aid of heat, in a flask, which was usually closed with a cork fitted with a set of potash bulbs, to prevent the absorption of carbonic dioxide by the alkaline liquid, but this precaution was not absolutely necessary. The solution, after it had cooled, was treated with twice or three times its volume of alcohol, and the mixture, after being thoroughly shaken, allowed to stand securely corked for about twenty-four hours. During this standing two layers were formed, a heavy aqueous solution, and a lighter alcoholic liquid. These were separated, the aqueous solution treated again with alcohol in the same way, and this extraction with alcohol repeated until the heavier portion solidified shortly after it had been removed from the alcohol, which happened usually after the third or fourth extraction. The crystalline mass thus obtained we have called fusible sodic zincate, because it melts below 100°. The second sodic zincate was obtained from the alcoholic washings, which were mixed, and allowed to stand in a corked flask, when after some time, which varied from a few hours to several days, white crystals were deposited on the sides of the flask, which gradually increased in quantity. The formation of these crystals did not occur invariably, but they could often be made to appear by adding more alcohol to the washings. This compound deposited from the alcoholic washings does not fuse even at 300°, and we shall call it infusible sodic zincate.

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* The sodic hydrate used by us had been purified by alcohol.

Analysis of the Fusible Sodic Zincate, $Zn_3O_6Na_4H_2 . 17 H_2O$.

This substance is the principal product of the reaction, forming, as nearly as we could estimate, over 90 per cent of the total product. Since both water and alcohol decompose it, a further purification seemed impossible, and we were obliged to analyze it as it was obtained by the precipitation with alcohol, simply drying it by pressure between filter paper under heavy weights.

The method of analysis, which we adopted after trying several others, consisted in dissolving the substance in dilute sulphuric acid, and precipitating the zinc by means of a measured quantity of a standard solution of sodic carbonate. The zinc was weighed as oxide. The filtrate was acidified with sulphuric acid, evaporated to dryness, weighed, and then the amount of sodium calculated after subtracting from the total weight of the sodic sulphate the weight of sodic sulphate corresponding to the sodic carbonate added.

I. 0.4720 grm. of the substance gave 0.1744 grm. of zincic oxide and 0.2080 grm. of sodic sulphate.

II. 0.6420 grm. of the substance gave 0.2302 grm. of zincic oxide and 0.2718 grm. of sodic sulphate. 0.8802 grm. of substance from the same preparation lost at 240° 0.3920 grm. of water, and the dried product gave on heating with chromic oxide in a stream of dry oxygen 0.0342 grm. of water.

III. 0.9682 grm. of the substance gave 0.3370 grm. of zincic oxide and 0.3992 grm. of sodic sulphate. 0.8770 grm. of substance from the same preparation lost at 240° 0.4021 grm. of water.

	I.	II.	III.
Zinc	29.66	28.78	27.93
Sodium	14.28	13.72	13.36
Water		44.54	45.83
Constitutional Water		3.88	

Each of these three analyses was made with a sample from an entirely separate preparation, in order to determine whether the substance had a definite composition, and when it is remembered that it could not be purified by crystallization, and was dried only imperfectly by pressing with filter paper, the agreement is as close as could be expected; but it is obvious that in a case like this the atomic ratios are of much more importance than the percentages, and we have accordingly calculated them as follows.

Atomic Ratio of Zinc to Sodium in Fusible Sodic Zincate.

	Zinc	:	Sodium.
I.	1.	:	1.36
II.	1.	:	1.35
III.	1.	:	1.35

The agreement between these numbers proves conclusively that the substance is a definite compound, and that the proportion of zinc to sodium is as three to four. In trying to calculate a formula for it, we have felt much doubt in regard to the amount of water of crystallization for the reasons given above; but the one finally adopted by us gives percentages which agree so well with those found, that it cannot be far from the truth, especially as the amounts of water found are about as much higher than those calculated as was to be expected. The constitutional water, on the other hand, comes very high, but we do not have much faith in this determination.

	Calculated for		Found.	
	$Zn_3O_6Na_4H_2$ 17 H_2O.	I.	II.	III.
Zinc	28.28	29.66	28.78	27.93
Sodium	13.30	14.28	13.72	13.36
Water	44.24		44.54	45.83
Constitutional Water	2.60		3.88	

To prove that the substance contained water, and not alcohol of crystallization, a combustion of it was made in the usual manner, but only a mere trace of carbonic dioxide was obtained.

The formula of this substance, $Zn_3O_6Na_4H_2 . 17 H_2O$, agrees, except in water of crystallization, with that of the substance analyzed by Malaguti (see page 15), which, written in the same way, becomes $Zn_3O_6(NH_4)_4H_2 . 9 H_2O$. This, as has been mentioned already, is the only zincate of which an analysis has been published.

We have made only one analysis of another preparation of this substance, which is comparable to those given above; this gave about the same percentage of zinc, 29.45, but a much larger amount of sodium, 19.56, which was undoubtedly due to a small quantity of sodic hydrate left adhering to the crystals, as this was the first preparation we made, and therefore was not pressed out so thoroughly as the later ones, after we had become more familiar with the manipulation.

Properties of the Fusible Sodic Zincate.

The substance as precipitated by alcohol from its solution in aqueous sodic hydrate forms a white mass, made up of radiating crystals, often of considerable size. It fuses at about 70°, but, owing to the difficulty of drying it, no attempts were made to determine the melting point accurately. Water decomposes it rapidly and completely, converting it into a white insoluble powder, which gave on analysis the following result.

0.1990 grm. of the substance gave 0.1910 grm. of zincic oxide and no sodic sulphate.

	Calculated for		Found.
	ZnO_2H_2.	ZnO.	
Zinc	65.72	80.28	77.03

The substance therefore seems to be principally zincic oxide mixed with a slight impurity of the hydrate. Alcohol decomposes it in a similar way, but more slowly, as is shown by the following percentages obtained from the analyses of two preparations (IV., V.), which we had attempted to purify by washing with alcohol.

	III.	IV.	V.
Zinc	27.93	29.96	33.36
Sodium	13.36	12.27	10.48

III. is one of the analyses already given. The substance for this analysis was only pressed with filter paper. IV. was a sample which had been washed three times with common alcohol, while the substance which had the composition given under V. had been washed four times with absolute alcohol. These numbers show that the action of the alcohol consists in gradually removing the sodium as sodic hydrate, and this point is brought out even more sharply by a comparison of the atomic ratios.

	Zinc	:	Sodium.
III.	1.		1.35
IV.	1.		1.16
V.	1.		0.89

It follows from what has been said on this subject, that care must be taken not to continue longer than is absolutely necessary the treatment with alcohol during the preparation of the sodic zincate. Although the substance is decomposed by both alcohol and water, it seems to exist during the process of manufacture dissolved in a mixture of these solvents in presence of an excess of sodic hydrate, an observation which is confirmed by that of Prescott (see page 15). It is insoluble in ether, and absorbs carbonic dioxide rapidly from the air. At 100° it loses only 12 molecules of its water of crystallization, as is shown by the following analysis.

0.4720 grm. of the substance analyzed under I., when heated to 100° in a stream of pure dry air, lost 0.1510 grm. of water.

	Calculated for a loss of $12H_2O$.	Found.
Water	31.23	32.00

Analyses and Properties of the Infusible Sodic Zincate, $(ZnO_2NaH)_2 . 7 H_2O$.

This substance, which crystallizes from the alcoholic washings obtained in the preparation of the fusible compound just described, is formed in comparatively small quantities. As nearly as we could estimate, only a few per cent of the total product consisted of it. As, like the fusible compound, it is decomposed by both water and alcohol, no attempt was made to purify it further, but it was analyzed after drying at ordinary temperatures by the method already described (see page 17).

I. 0.7470 grm. of the substance gave 0.3424 grm. of zincic oxide and 0.2913 grm. of sodic sulphate; 0.4762 grm. of substance from the same preparation lost at 220° 0.1637 grm. of water.

II. 0.6044 grm. of the substance lost at 300° 0.2066 grm. of water, and gave 0.2700 grm. of zincic oxide and 0.2355 grm. of sodic sulphate.

	Calculated for	Found.	
	$(ZnO_2NaH)_2 7H_2O$.	I.	II.
Zinc	35.32	36.78	35.86
Sodium	12.50	12.62	12.62
Water	34.24	34.37	34.19

The considerable difference between the percentages of zinc is not greater than was to be expected, when the impossibility of purifying the substance is remembered. Each of these analyses was made with a sample from a separate preparation, and we add the following analysis, made early in the work simply to determine the ratio between the zinc and sodium, no care having been taken to dry the substance.

III. 0.7025 grm. of slightly moist substance gave 0.2260 grm. of zincic oxide and 0.1951 grm. of sodic sulphate.

The percentages derived from this analysis are of course of no value, but it gives an atomic ratio which agrees with those from the preceding analyses so closely that there can be no doubt that this substance possesses a definite composition.

Atomic Ratio of Zinc to Sodium in the Infusible Sodic Zincate.

	Zinc	:	Sodium.
I.	1.03		1.
II.	1.03		1.
III.	1.02		1.

A combustion of the substance showed that it contained no alcohol.

This substance undoubtedly corresponds to the crystalline body obtained by Fremy (see page 15), who assigned to it the same ratio between the zinc and potassium. Laux (see page 14), on the other hand, ascribed to his crystals, which were soluble in water, the formula ZnO_2K_2, but stated that upon heating these crystals he obtained an amorphous powder, which showed the ratio of 1 : 1 between zinc and potassium ; that is, the same obtained in the crystals by Fremy and us. We have met with no substance corresponding to the soluble crystals of Laux.

Properties. — The infusible sodic zincate crystallizes from a solution in dilute alcohol containing an excess of sodic hydrate in white needles, sometimes over a centimeter long, forming loose radiating groups usually of a conical shape, but occasionally circular or spherical. It does not melt even at 300°, and is decomposed by alcohol, or water, if these solvents are free from sodic hydrate, absorbs carbonic dioxide from the air, but much less rapidly than the fusible compound, and does not lose the whole of its water of crystallization until heated above 200°.

We have not succeeded in finding any other definite compound among the products of the action of sodic hydrate on zincic oxide, and, if any other exists, it can be only in very small quantity.

After we had settled the composition of the sodic zincates, we turned our attention to the study of other zincates, and also tried some experiments with magnesic oxide. The results of all this work were negative, but nevertheless we think it best to give a brief statement of what we have done.

In all our attempts to prepare potassic zincate we encountered the difficulties already mentioned by Fremy; in fact, we have not succeeded in obtaining in any experiment the crystals described by him, although we have modified the process employed in a number of different ways; but the solution of zincic oxide in potassic hydrate, when treated with alcohol according to the method which had yielded such good results with sodic zincate, gave only amorphous precipitates, which looked like zincic oxide, but were not wholly free from potassium; as the absence of crystalline form left us no means by which we could judge of the purity of this substance, we did not think it worth analysis.

With ammonic hydrate the results looked more promising at first, as the solution of zincic hydrate in ammonic hydrate occasionally gave a small quantity of crystals, after it had been mixed with alcohol and allowed to stand; but in this case there was no separation of the liquid into two layers. These crystals looked very much like the infusible sodic zincate described above, but the analyses of four preparations showed that they had no constant composition, the following percentages being obtained.

	I.	II.	III.	IV.
Zinc	48.66	45.90		59.96
Ammonia	7.35	4.58	3.67	5.28

In view of these results, it did not seem worth while to continue the investigation.

In beginning this research we had hoped, by acting on the sodic zincate with a cobaltous salt, to obtain Rinman's green, and in this way throw some light on the composition of this pigment. These hopes have not been fulfilled, as the zincates were decomposed by alcohol or water, as already stated, and therefore the action could not be carried on in solution, and the melted fusible zincate, when treated with cobaltous chloride, gave only a blackish precipitate with no shade of green. The same result was obtained when an ethereal or absolute alcohol solution of cobaltous chloride was allowed to act on the zincate. We have also made many attempts to purify Rinman's green, prepared according to the usual method, in order to fit it for analysis, but none of these have succeeded, the substance being decomposed by solutions of alkalis or acids, in fact even by a solution of carbonic dioxide under pressure, which dissolved both zincic and cobaltous carbonates, and finally left a blackish gray residue.

Although magnesic hydrate does not dissolve in sodic hydrate under ordinary conditions, we thought that possibly a very strong solution of sodic hydrate might have some solvent action at its boiling point, and, upon trying the experiment, obtained long prismatic crystals, which, however, we found contained only a mere trace of magnesium (0.39 per cent), and consisted of the crystallized sodic hydrate recently obtained by Cripps,* as shown by the following analytical results.

I. 0.5620 grm. of the substance lost 0.2150 grm. of water.
II. 0.4115 grm. of the substance gave 0.4585 grm. of sodic sulphate.

	Calculated for	Found.	
	$(NaOH)_3 4 H_2O$	I.	II.
Water	37.50	38.26	
Sodium	35.93		36.11

The curious point about this observation, which alone makes it worth recording, is that the solution of sodic hydrate used could not be made to crystallize before it was treated with magnesic oxide, but after such treatment crystallized so rapidly that it was impossible to filter it. The experiment was repeated several times, each time with the same result. What the cause of this difference in behavior may be we have been unable to determine, but think that possibly a small quantity of sodic carbonate in our solution of sodic hydrate may have prevented the crystallization, which took place as soon as this was converted into hydrate by the magnesic oxide.

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* Pharm. Jour. Trans., Ser. 3, xiv. 833 (1884).